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by

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16. ABSTRACT The paper gives results of an experimental investigation into the waste properties and kiln parameters that determine both the instantaneous intensity and total magnitude of transient puffs leaving the kiln. (NOTE: The batch introduction of waste-filled drums or containers into practical rotary kiln incinerators can lead to transient overcharging conditions, refered to here as puffs.) The experimental apparatus utilized was a 73 kW laboratory rotary kiln simulator. Surrogate solid wastes in the form of plastic rods and surrogate liquid wastes on sorbents in cardboard containers were investigated. A statistically designed parametric study was used to determine the extent to which waste and kiln variables (e.g., charge mass, charge surface area, charge composition, kiln temperature, and kiln rotation speed) affected the intensity (hydrocarbon peak height) and magnitude (hydrocarbon peak area) of puffs. Results demonstrate the relative ease with which puffs are achieved, even at high excess air values and high kiln temperatures. Puffs from even innocuous surrogate wastes can contain a number of hazardous compounds. Increasing kiln temperature can cause an adverse effect on puff intensity, probably due to increased devolatilization rates. There are large effects of waste composition and, for solid wastes, their surface areas are critical variables.

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Paper — Parametric Studies Delineating the Occurrence of Transient Puffs in a Rotary Kiln Simulator

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Abstract — The batch introduction of waste-filled drums or containers into practical rotary kiln incinerators can lead to transient overcharging conditions, which, for brevity, are here denoted as "puffs." This paper describes results of an ongoing experimental investigation at the U. S. Environmental Protection Agency into the waste properties and kiln parameters that determine both the instantaneous intensity and the total magnitude of transient puffs leaving the kiln. The experimental apparatus utilized was a 73 kW (250,000 Btu/hr) laboratory rotary kiln simulator. Surrogate solid wastes in the form of plastic rods and surrogate liquid wastes on sorbents in cardboard containers were investigated. A statistically designed parametric study was used to determine the extent to which waste and kiln variables (such as charge mass, charge surface area, charge composition, kiln temperature, and kiln rotation speed) affected the intensity (hydrocarbon peak height) and magnitude (hydrocarbon peak area) of puffs.

Results demonstrate the relative ease with which failure conditions are achieved, even at high excess air values and high kiln temperatures. Puffs arising from even innocuous surrogate wastes can contain a number of hazardous compounds. Increasing kiln temperature can cause an adverse effect on puff intensity, probably due to increased devolatilization rates. There are large effects of waste composition, and, for solid wastes, their surface areas are critical variables.

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Introduction

Rotary kiln incinerators may comprise one of the most versatile and most universal waste disposal systems available, and therefore are featured prominently in this conference on Operating European Hazardous Waste Management Facilities. Available data (Fabian et al. 1979, Bonner et al. 1981) indicate that these systems are generally safe and effective. However, most data on destruction and removal efficiencies (DREs) of many hazardous wastes have been obtained under steady-state operating conditions, and little information is available on potential problems under the transient overcharging conditions that occur when drummed or solid materials are batch fed into the combustion chamber. These transient overcharging conditions can occur if waste parameters are not properly matched to the incinerator operating conditions. They can lead to heavy loads on the afterburner and downstream gas cleanup systems. For the sake of brevity, we denote this transient condition as a "puff."

This paper describes results of a research program currently being conducted at the U. S. Environmental Protection Agency research laboratories in North Carolina, USA. The overall objectives are to gain engineering insight into potential problem areas related to rotary kiln incineration, with a view to developing predictive methods that correlate possible failure modes to waste characteristics and kiln operating parameters using continuous on-line instrumentation. The specific problem addressed in this paper is that of transient puffs originating from the batch introduction of either solids or liquids on sorbents in containers.

The problem is approached through parametric experimentation on a laboratory kiln incinerator simulator. The value in utilizing a prototype rotary kiln simulator, rather than an actual permitted field device, lies in its ability to allow parametric variation, in a controlled fashion, without loss of the overall complicated salient feature of practical kiln operation. Thus, this research neither focuses primarily on DREs of specific principal organic hazardous constituents (POHCs) nor evaluates any specific rotary kiln incinerator design. Rather, it delineates, in a generic sense, fundamental combustion phenomena that are important in the formation of transient puffs and worthy of further study.

It is hypothesized that a waste parameter of direct importance in the generation of transient puffs is the volatility, or the rate of volatiles release, of the waste. When devolatilization occurs rapidly, local oxygen concentrations in the flue gas are almost totally depleted or displaced by the volatilized waste species. A transient puff then moves as a plug through the system. When volatiles are released slowly, however, they bleed into the flue gas stream without totally depleting the local oxygen levels, allowing more complete oxidation to occur and puffs to be minimized. Therefore, a major focus of the research results presented here is on the effects caused by differences in waste volatility. Specifically, we compare results from the batch introduction of surrogate solid wastes, in the form of plastic rods, to those resulting from contained surrogate liquid/sorbent wastes.

The paper is divided into three parts. First the rotary kiln simulator is described, its performance characteristics are compared to full-scale units, and the facility is validated as a useful laboratory prototype of a rotary kiln incineration process. Then, results of parametric studies delineating the occurrence of transient puffs resulting from the batch introduction of prototype solid plastic wastes into the kiln are described. The third part describes analogous results for the batch incineration of liquid/sorbent mixtures in cardboard containers.

Laboratory Rotary Kiln Simulator

Field rotary kiln incineration systems have been described elsewhere (Fabian et al. 1979, Tanner 1979). In general, they are designed to handle the following processes: gaseous and pumpable wastes can be continuously introduced into the kiln through standard burners, while solid material and liquid filled drums or containers can be fed through entrance chutes, either cocurrently or countercurrently with the gas flow. Kiln rotation continuously exposes fresh surfaces for oxidation and provides for constant ash removal. Kiln angle and rotation determine the solids residence time and ensure complete destruction of the contents of steel drums. Noncombustible residues are usually water quenched and removed by conveyor for landfill. A secondary combustion chamber with an afterburner is usually provided for further destruction of unburned gaseous and suspended particulate organics. Together, the rotary kiln and afterburner provide turbulent mixing of

the waste species with excess oxygen at high temperatures and for residence times sufficient to destroy the organic waste to within tolerable levels. Combustion gases are then quenched and scrubbed of acid and particulates before discharge into the environment. When drummed or solid materials are batch fed into the combustion chamber, they are typically charged at a rate of 6 to 12 containers per hour.

The EPA laboratory kiln simulator, used in the research reported here, was designed to contain the salient features of practical full-scale kilns, as described above and shown on Table 1, but still remain sufficiently versatile to allow parametric experimentation by varying one parameter at a time, or by controlling a set of parameters independently.

A schematic view of the simulator is shown on Figure 1, and its overall characteristics are compared to those of full-scale units in Table 1. A detailed description of the hardware specifications has been presented by Linak et al. (1986). Rated at 73 kW (250,000 Btu/hr), the simulator consists of five steel-shelled refractory-lined sections (kiln, transition/afterburner, backfire burner, control temperature tower 1, and control temperature tower 2) as shown on Figure 1. Internal radial dimensions vary from 0.762 m (30 in.) in the kiln recess to 0.456 m (18 in.) in the transition and tower sections. Outside diameters vary from 1.168 to 1.219 m (46 to 48 in.). Internal axial dimensions total 6.1 m (240 in.) from the front burner wall to the point of dilution air addition.

Surrogate waste materials are batch charged through a sliding gate/ram assembly located on the transition/afterburner section (Figure 1). After solids or contained liquids are placed in the charging basket, the gate is opened and the basket is rammed into the kiln. At the mechanically set stop position, the basket is stopped and the momentum carries the charge into the kiln recess. The basket is then withdrawn and the gate closed. A cover over the charging assembly minimizes air infiltration into the kiln. The entire charging operation typically takes less than 4 seconds.

Quantification of a system upset condition (puff) requires the realtime measurement of system variables. Peak responses of fixed gas and hydrocarbon analyzers indicate extremes. Other useful variables include time-integrated responses (in particular, the time-integrated response of the total volatile hydrocarbon analyzer).

Table 1. Rotary kiln characteristics, full-scale vs EPA simulator.

	Full-Scale	EPA Simulator
Heat Input, kW (Btu/hr)		
Mean	10431 (35.6E+06)	73 (0.25E+06)
Median	3018 (10.3E+06)	
Heat Release, kW/m^3 ($Btu/hr \cdot ft^3$)	155-414 (15,000-40,000)	259 (25,000)
Kiln Exit Temperature, K (°F)		
Range	533-1533 (500-2300)	1089-1366 (1500-2000)
Typical	922-1144 (1200-1600)	
Afterburner Exit Temperature, K (°F)		
Range	1144-1811 (1600-2800)	1366-1477 (2000-2200)*
Typical	1366-1589 (2000-2400)	
Kiln Residence Time		
Solids, hr	< 2	N/A
Gases, sec	1-3	2-3
Afterburner Residence Time, sec		
Range	1-4	3-4*
Typical	2	
Excess Air, percent		
Range	75-210 (SR=1.75-3.10)	10-200 (SR=1.10-3.00)
Rotational Speed, rpm	0.25-1.5	0.1-3.0
Peripheral Speed, m/min (ft/min)	0.305-1.524 (1-5) (outer surface)	0.244-7.010 (0.8-23) (inner surface)
Length to Diameter Ratio		
Range	2-10	0.8 (recess)
Typical	3-4	3.8 (overall)
Angle to Horizontal, percent	< 2-3	0 (no rake)
Auxiliary Fuel, kg/hr (lb/hr)	Natural Gas or Fuel Oil (none typically used)	Natural Gas 5.22 (11.5) (always used)
Feed Capacity		
Solids, kg/hr (lb/hr)	600-2000 (1320-4410)	
Liquids, l/hr (gal./hr)	630-2250 (165-590)	

* Data presented does not include the use of the afterburner system.

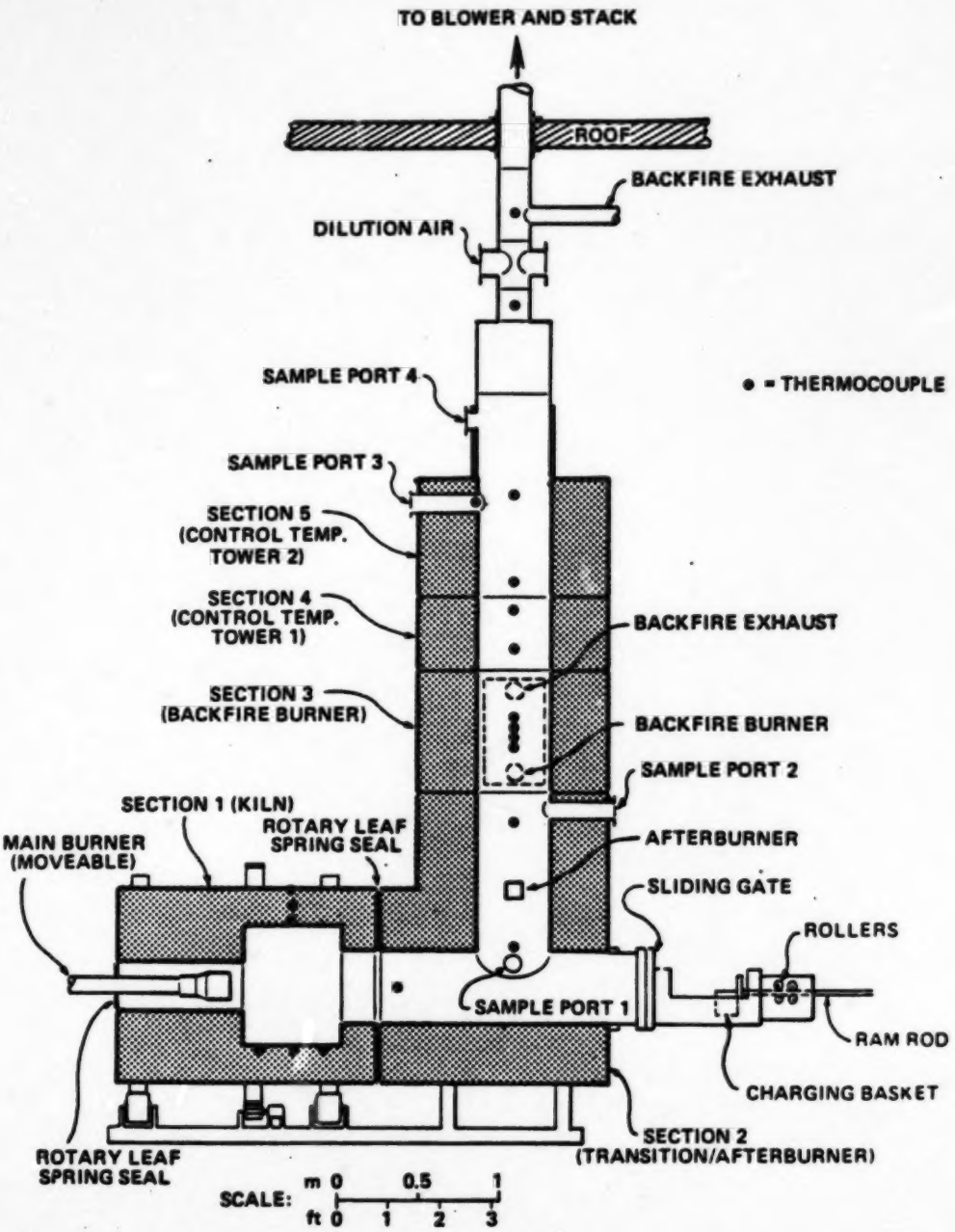

Figure 1. EPA rotary kiln incinerator simulator.

This method permits a determination of emitted mass. By holding constant sampling temperatures, pressure, and flow rates, a constant volumetric flow is delivered to the analyzer's flame ionization detector (FID). Provided the incinerator flue gas flow rate is constant and the gases well mixed, the integrated mass measured is then proportional to the total mass of volatile hydrocarbons passing up the stack during a puff. The peak response, on the other hand, represents the maximum concentration in a puff.

This paper is concerned only with phenomena occurring in the kiln (primary combustion chamber); so samples withdrawn represent effluent leaving the kiln and entering the afterburner (secondary combustion chamber). Throughout this work, there was neither supplemental heating nor afterburning downstream of the kiln exit. Samples were withdrawn at sample port 4 (Figures 1 and 2), and extractive sampling and analysis procedures can be found elsewhere (Linak et al. 1986). The results will allow us to determine the inlet transient conditions with which an afterburner must be capable of dealing, and how these depend on kiln and waste parameters.

Table 1 presents a comparison between the operating characteristics of the EPA simulator and those of full-scale rotary kiln incinerators as reported by Frankel et al. (1983), Bonner et al. (1981), and the trade literature. The simulator matches the volumetric heat release and the gas-phase residence times of full-scale units, but is rated at less than 5 percent of the gross heat input of full-scale units.

Figure 2 shows the axial time/temperature profile through the kiln and the subsequent control temperature tower (without additional heat addition) under the low and high firing conditions utilized in the parametric experiments reported in later sections. Measurements in the kiln were taken with a suction pyrometer with a type R thermocouple. Gas phase temperatures range from 1258 K (1804 °F) to 1056 K (1440 °F) after 3.6 seconds at the kiln exit and from 1383 K (2030 °F) to 1327 K (1928 °F) after 3.1 seconds under low and high firing conditions, respectively. These gaseous time/temperature profiles simulate full-scale units well (Table 1).

An apparent discrepancy between the simulator design and that of full-scale systems lies in the presence of the cavity in the simulator (not present in full-scale units), and in the resulting apparent discrepancy in L/D ratio

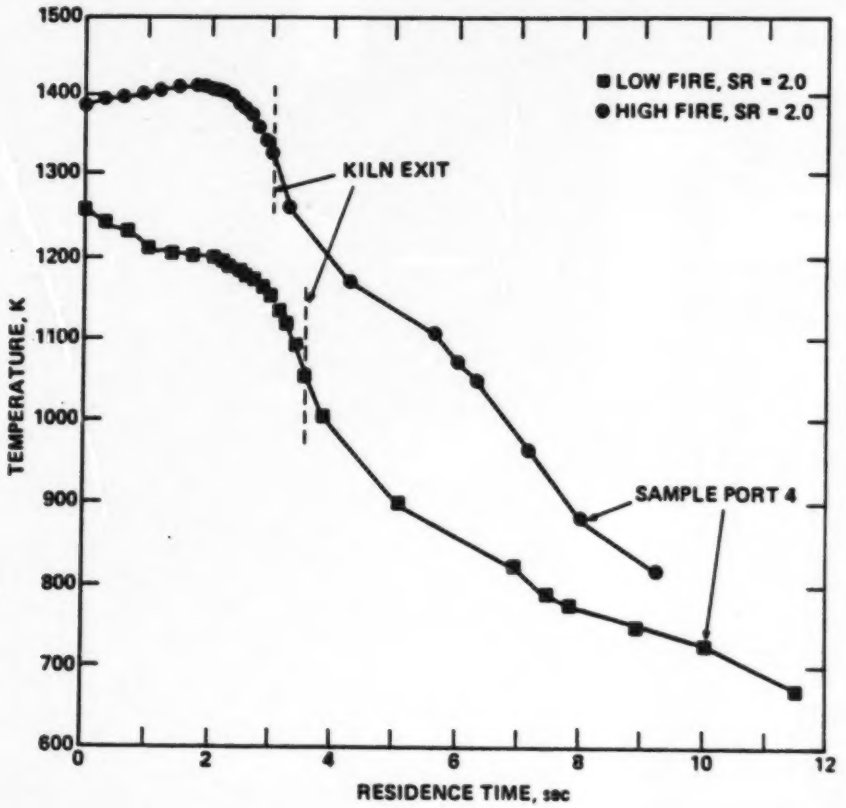

Figure 2. Temperature profile vs residence time, low and high fire test conditions.

(see Table 1). However, this discrepancy is more apparent than real for the following reasons. First, the simulator does not attempt to reproduce the actual continuous travel of solids along the kiln bottom, but rather simulates this by using a control volume approach in which the solids reside in the cavity and the burner can be continuously moved. In this way, the distance between a charge and the heat release zone can be increased (simulating counter-current flow), and the overall residence time of the solid charge is determined by the length of the batch experiment. Thus, the kiln L/D ratio, which (together with slope and rotation speed) normally determines the solids residence time in a practical kiln (Brunner 1981), is not important for this purpose as far as the simulator is concerned.

Of critical interest in the determination of transient puff generation is the contacting between the waste or waste products and the main combustion flue gas. It might be argued that the presence of the cavity might exacerbate a poor mixing problem and thus artificially yield puffs, where none might exist in the field. To test whether improved contacting decreases the magnitude of transient puffs, experiments were conducted in which the rotation speed was changed from 0 to 3 rpm. These tests conclusively showed that improved contacting achieved by increasing rotation speed yielded larger puffs. Therefore, the tests in which the baseline rotation speed was 1 rpm yield conservative results, and the generation of the puff in the simulator is not an artifact due to poor contacting or the presence of the cavity.

Results

Preliminary Tests

Preliminary tests were conducted during the shakedown of the rotary kiln simulator to examine the operating parameters that would promote emission failure mode conditions (puffs) during the incineration of solid waste materials. These tests, which utilized 3.79 l (1 gal.) wide-mouthed polyethylene (PE) bottles, demonstrated that transient overcharging conditions or puffs could be easily achieved. These puffs lasted approximately 45 seconds and led to volatile hydrocarbon concentrations in excess of 20,000 ppm and black smoke. Furthermore, the preliminary tests allowed us to formulate the hypothesis that, for a given solid waste compound, the occurrence and magnitude of a transient puff

depended on charge mass, charge surface area, and kiln temperature.

Waste composition was also hypothesized to be a most important factor in determining the occurrence and magnitude of puffs. Experimentation was therefore divided into two phases: Phase 1 was concerned with well-defined prototype solid plastic wastes; and Phase 2 dealt with liquids absorbed on sorbents in cardboard containers.

Statistical Design of Experiments

In both experimental phases, the general methodology employed was that of response surface experimentation (Hicks 1973). This methodology allows one to determine, on the basis of one experiment involving a minimal number of trials, how to adjust the parameter settings for the next experiment in order to move most quickly to those settings which optimize a response. In addition, once having located the optimal or near optimal parameter settings, the procedure allows determination of a quadratic equation which relates the response to the controlled parameters in a region surrounding this optimal point.

For both phases of experimentation, low, intermediate, and high settings of the variables to be investigated were determined. For Phase 1, dealing with prototype solid plastic wastes, these variables were charge mass, charge surface area and kiln temperature. For Phase 2, which was treated separately and concerned with liquid on sorbent wastes, these variables were charge mass, kiln temperature, and kiln rotation speed.

Each phase involved four waste compositions and consisted of at least 24 trials. This allowed quadratic models to be formulated as well as full degree of freedom tests of significance of all main effects and all two-factor interactions (Hicks 1973). Each trial involved between 5 and 10 replicates, depending on the response variance and the availbility of waste material. Replicate values of FID measurements of time-resolved total hydrocarbon peak area and peak height were averaged. A quadratic response surface model was fitted to the mean values using weighted least squares. The quadratic model included linear and quadratic dependencies on each variable, as well as all the cross-product terms denoting interactions between pairs of variables. The pre-programmed procedures in SAS (Statistical Analysis

System), which are relevant to response surface methodology, were used further to interpret the data. Similarities in model coefficients between different wastes (within one phase of experimentation) were statistically tested for evidence that dependencies of the response on various parameters altered from waste to waste. Further tests denoted which linear, quadratic, or interaction dependencies were statistically significant.

Prototype Solid Plastic Wastes

Plastic rods composed of low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), and polyvinylchloride (PVC) were chosen as prototype plastic wastes. These rods had well defined initial shapes and allowed, within a certain range, for surface area and mass to be varied independently by varying rod diameters. The plastics span a range of molecular structures, molecular weights, and elemental compositions that are of intrinsic interest to the incineration community.

The representative kiln temperature used as a control parameter was that measured by a bare type K thermocouple at the kiln exit, 0.97 m (38 in.) from the front burner wall. Low and high fire conditions were used and correspond to the two temperature distributions in Figure 2. The remaining important kiln parameters were: stoichiometric ratio of 2.0 or excess air of 100 percent; and rotation speed, 1 rpm. High fire conditions were obtained by making use of the thermal inertia of the kiln to heat the flue gas to a temperature greater than that occurring naturally at SR=2, as shown on Figure 2.

During the test program, a shortage of some materials forced minor modifications of the statistically designed test matrix. However, these modifications were more than compensated for by additional tests, as summarized on Figure 3. The dashed straight lines define the experimental domain accessible using LDPE rods of specified diameters. Analogous lines for other plastics are not shown, for the sake of clarity. In general, charge mass and surface area are not independent; however, within a restricted domain it was possible to vary charge surface area for a given charge mass by changing rod diameter alone. While Figure 3 includes all test points examined in this phase (37 total), the actual statistical test matrix is confined to a smaller area defined by the region within the dotted lines.

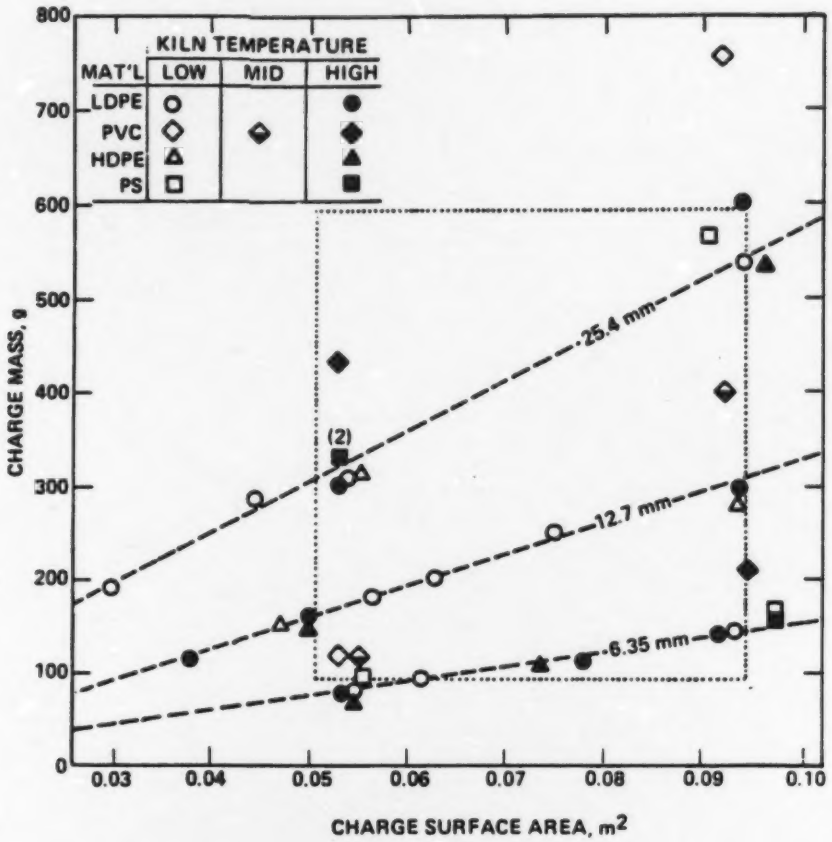

Figure 3. Test conditions for solid plastic rods.
Dashed lines define domain accessible to LDPE rods of specified diameters.
Dotted lines define boundries of response surface plots.
Each trial consisted of 5 to 10 replicate tests.
Duplicate trials denoted by (2).

The area under the transient curve measured by flame ionization detection (FID) is, under constant sampling conditions, proportional to the total quantity of volatile hydrocarbon in a puff. Peak height, on the other hand, represents the instantaneous volatile hydrocarbon concentrations in the puff. The volatile hydrocarbons are defined as those sampled at 420 K (300 °F) and analyzed by continuous FID. Figure 4 shows typical traces for two different plastics at similar test conditions. Clearly there are significant quantitative and qualitative variations in the mechanisms generating transient puffs from solid wastes of differing compositions. There was some variation in results from replicate tests, but this is to be expected from experimentation on equipment of this complexity.

Statistical analysis yielded a model in which the response (peak area, μg as CH_4) was proportional to temperature, mass, surface area times mass, surface area times temperature, and mass times temperature. The weights used for the weighted least squares analysis were equal to the number of replicates for each trial. This model, which accounted for 95.9 percent of the variation among the 37 means (36 independent conditions and 1 duplicate), is described pictorially through the response surface plots shown in Figure 5 for the LDPE rods. Analogous contour plots for HDPE were similar, while those for the PS and PVC contained some similarities but also some significant differences.

Figure 5 illustrates that, for LDPE, the largest puffs (mass basis) occur at large surface areas and high charge masses. There exists a threshold charge mass, above which puffs rapidly appear, and this threshold is not sensitive to kiln temperature. For LDPE, charge surface area is important, and, within a certain charge mass range, can also determine the presence and magnitude of a puff. Increasing kiln temperature decreases the total volatile hydrocarbon species contained in a puff. This significant result was also true for the HDPE, PS, and PVC wastes. PS and PVC wastes, however, showed little effect of surface area on the integrated traces.

Data for maximum peak heights, representing the maximum instantaneous intensity of the puff, were analyzed statistically using the same procedures. The resulting quadratic model accounted for 84.3 percent of the variability of the 37 averaged data points used and is significantly different from the model for peak area. This demonstrates the importance of distinguishing between total mass of the puff and

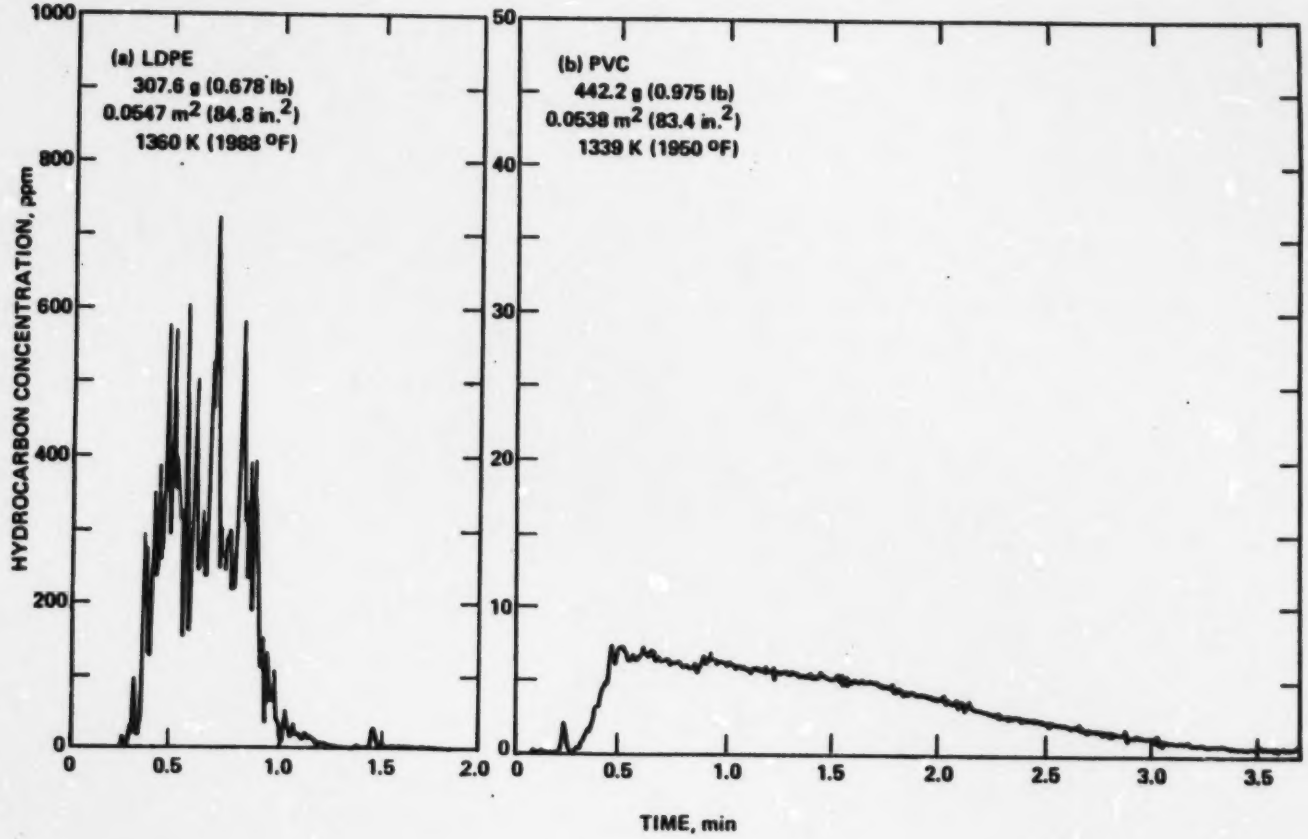

Figure 4. Comparison of LDPE and PVC transient hydrocarbon peak shapes at similar trial conditions.

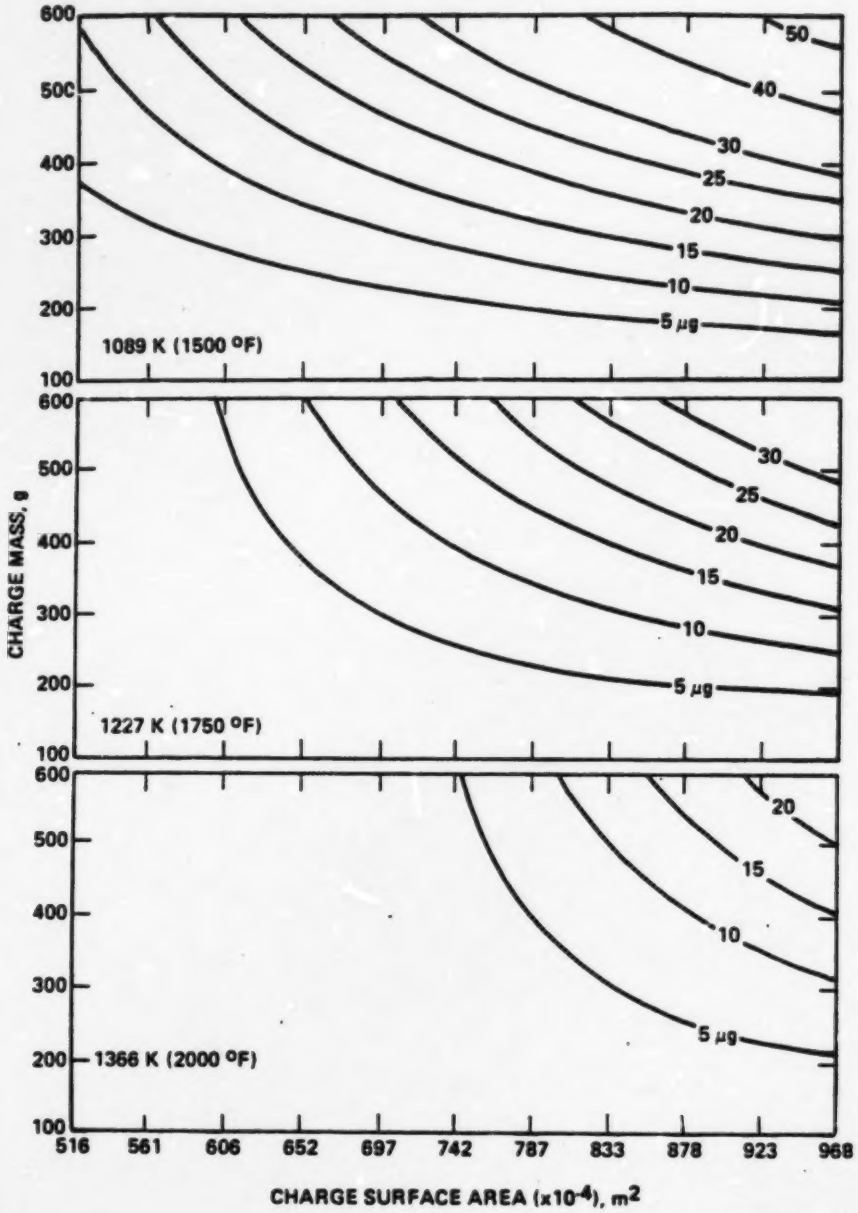

Figure 5. Effect of charge mass, charge surface area, and kiln temperature on integrated LDPE peak area. (Contour values denote total volatile hydrocarbons measured as micrograms of methane.)

the peak transient concentration. The resulting contour plots for LDPE are shown in Figure 6 and yield the important result that increasing the kiln temperature increased the maximum instantaneous concentration of volatile hydrocarbons emitted, which is contrary to the school of thought that destruction efficiencies necessarily increase with temperature. Charge surface area is very significant at lower kiln temperature, but less so at higher kiln temperatures. PS and PVC peak heights showed strong surface area effects, but the role of kiln temperature was then more ambiguous. For the PVC waste, peak heights were very much smaller, and peak durations very much longer than those for the HDPE and LDPE wastes at similar test conditions (see Figure 4).

It is likely that the formation of puffs from solid plastic wastes is governed by a number of related chemical and physical processes. High kiln temperatures enhance rapid devolatilization of the solids, thus increasing the rate of formation of volatile gases to displace or deplete the excess oxygen from the main burner combustion air supply. This may explain the significant effect of kiln temperature on the maximum instantaneous concentration of hydrocarbons in the puff (peak height). It is interesting to note, however, that in all cases, increasing kiln temperature decreased the total mass of volatile hydrocarbons emitted (peak area). This points to the beneficial (and not unexpected) effects of high temperatures to enhance oxidation mechanisms. Clearly, definition of an optimum condition is not trivial. In practice, afterburners must be able to handle large instantaneous pulses of wastes from the kiln, and so the results on peak height are of practical significance.

That surface area appears to be an important parameter, under several conditions, indicates the importance of physical processes, such as heat transfer to the solid and devolatilization from the surface. Decreasing surface area of the solid usually decreased both the intensity of the puff and the total volatile hydrocarbon mass emitted. The exceptions to this occurred at high kiln temperature when heat transfer and subsequent devolatilization are both more rapid.

Heat transfer is clearly not the only important mechanism, since there were vast differences in behavior between waste types. Some of this is due to differences in physical transformations of the solid rods upon landing on the hot refractory surfaces. Certain plastics quickly melted and

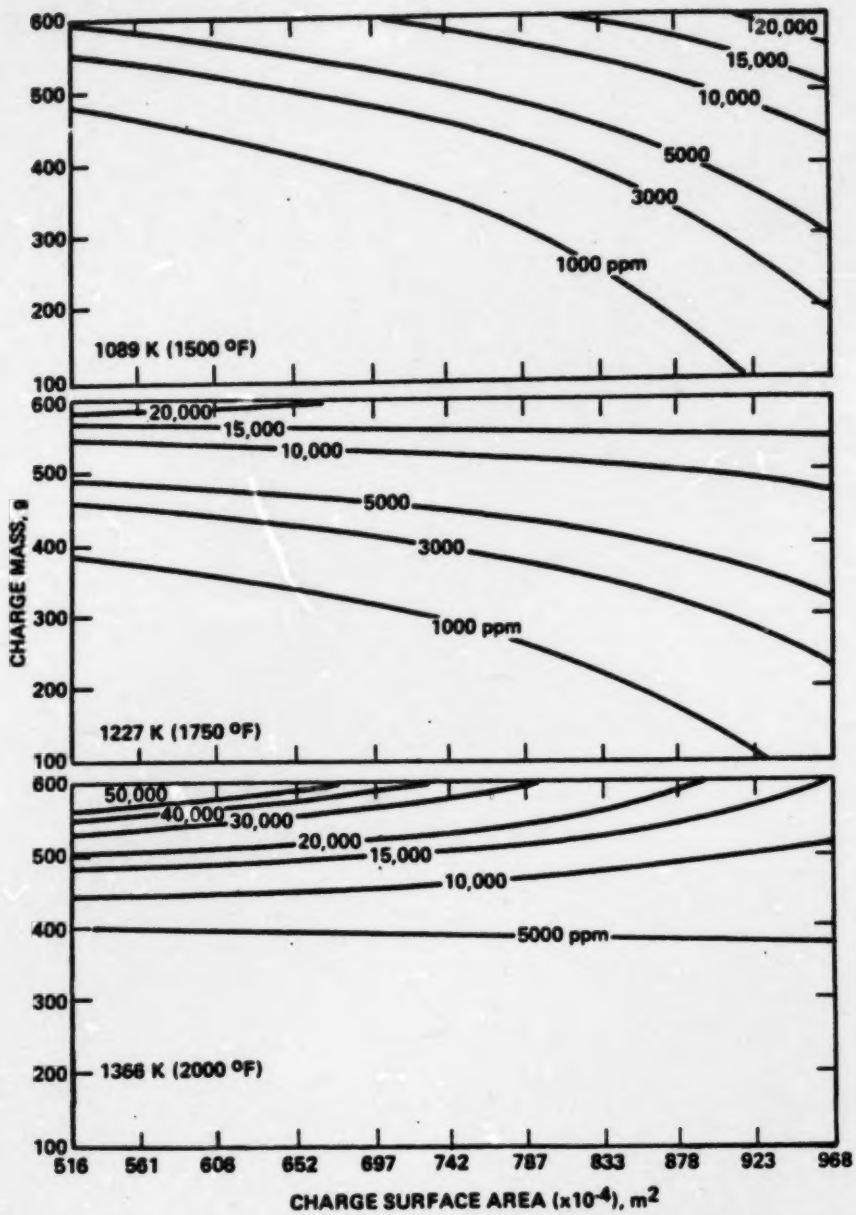

Figure 6. Effect of charge mass, charge surface area, and kiln temperature on absolute LDPE peak height. (Contour values denote peak volatile hydrocarbons measured as parts per million of methane.)

formed a pool, the surface area of which then had little to do with the initial surface area of the solid. PVC rods had the slowest rate of volatile release, for all surface areas, and therefore always formed the least intense, but longest puffs. Their effluent could be handled best by an afterburner. The PE wastes had the most rapid rate of volatile release, and thus are most likely to cause difficulties in the downstream afterburner. Clearly, volatile release rates are significant in characterizing the propensity of solid wastes to form transient puffs.

The composition of these transient puffs was also determined by stack sampling with VOST and SASS trains (Johnson and Merrill 1983, Johnson 1986), in conjunction with GC-MS analysis (James et al. 1985). Details on the conditions and sampling procedure have been described elsewhere (Linak et al. 1986). The results are shown on Table 2 and were significant in that they showed that hazardous constituents are contained in the puff, and that the more hazardous organo chlorides were detected when the waste consisted of PE/PVC mixtures but not in tests with PVC alone. This is consistent with the transient results described in the preceding paragraphs. PVC alone is devolatilized slowly, and forms small puffs of low intensity and magnitude. PE alone, on the other hand, forms intense puffs of great magnitude, but with no chlorine content. Therefore, the greatest likelihood of hazardous chlorinated hydrocarbons being formed occurs when PE and PVC are mixed. These tests also indicated that very small quantities of penta through octa chlorodioxins and furans were formed both from PE/PVC mixtures and from PVC alone (Linak et al. 1986).

Liquid/Sorbent Wastes

In practice, when liquids are incinerated in a batch mode, they are usually held on sorbents in containers or drums. In the research reported here, the containers consisted of 0.947 l (1 qt) closed, cylindrical cardboard vessels, with 135 g (0.298 lb) of shredded agricultural corncob as the sorbent. Prototype liquid wastes were toluene, No. 5 fuel oil, carbon tetrachloride, and methylene chloride. These compounds were chosen because they spanned a range of volatilities (the fuel oil, for example, required heating before being absorbed on the sorbent), and a range of chlorine substitution.

Table 2. Selected RCRA Appendix VIII compounds identified in test burns charging polyethylene and polyvinylchloride pipe.[x]

	Solvent Blank	Baseline* (a)	PE (b)	PE/PVC+ (c-1)	PE/PVC+ (c-2)	PVC (d)
(2-Ethylhexyl)phthalate		X	X	X	X	X
Naphthalene		X	X	X	X	X
Dichlorobenzene				X	X	X
1,2,4-Trichlorobenzene				X	X	
Hexachlorobenzene				X	X	
Pentachlorophenol				X	X	
Fluoranthene			X			

[x] In all cases, the kiln was at high fire conditions (1339 K, 1950 °F), 100 percent excess air (SR=2.0), 1 rpm kiln rotation, and 9 to 10 charges averaging 270 g (0.595 lb) each, were charged 1 every 10 minutes.

* Baseline test sampled auxiliary fuel combustion gas products; no waste material charged.

+ PE/PVC mixed charges were 50 percent each by weight.

A statistically correct experimental design was devised. This was identical to that used for the prototype solid wastes, except that the solids' surface area variable was replaced by kiln rotation speed, for which 0.5 and 2.0 rpm were the low and high values, respectively. Rotation speed was chosen because, like surface area for a solid, it directly influences contacting between waste and the surroundings. The kiln was operated, as before, at 100 percent excess air with high and low fire conditions as shown on Figure 2. Each test consisted of between 5 and 10 replicate charges, although reproducibility was much better for the liquids than for the solids. The total area and peak height of the time resolved traces of volatile hydrocarbons measured by the FID were recorded and are hereafter denoted simply as "peak area" or "peak height." Figure 7 shows typical traces for two different liquids at similar test conditions, and demonstrates, again, the significant quantitative and qualitative variations resulting from charge composition changes.

Quadratic models were fitted to the data using weighted least squares where the weights were now equal to the number of replicates divided by the variance between replicates. For peak area, the response models (exponentiated, to avoid negative values) contained linear terms in charge mass rotation speed and temperature and cross terms in rotation speed times mass and mass times temperature. They accounted for 99.35 percent of the variation in the response caused by changes in parameters. The resulting peak area contour plots for toluene are shown on Figure 8. In all cases, increasing the kiln rotation speed increased the peak area of the FID hydrocarbon trace. This was also true for all four liquids examined at all temperatures. The contours differ from those presented for the solids in at least two major respects. First, for this liquid, the peak area increased with increasing temperature. Second, at high rotation speeds and at high temperatures (i.e., at high peak area values), the measured areas appear to exhibit anomalous behavior in that the contours are concentrated at the lower left-hand corner, with a saddle contour. This behavior began when peak concentrations of volatile hydrocarbons exceeded 14000 ppm, and may be due to the fact that, at very high hydrocarbon loadings in the puff, soot formation is accelerated and the remaining volatile hydrocarbons measured by the FID no longer represent the total puff size. This quantity is better represented by the weight of condensibles collected on the FID sample line filters.

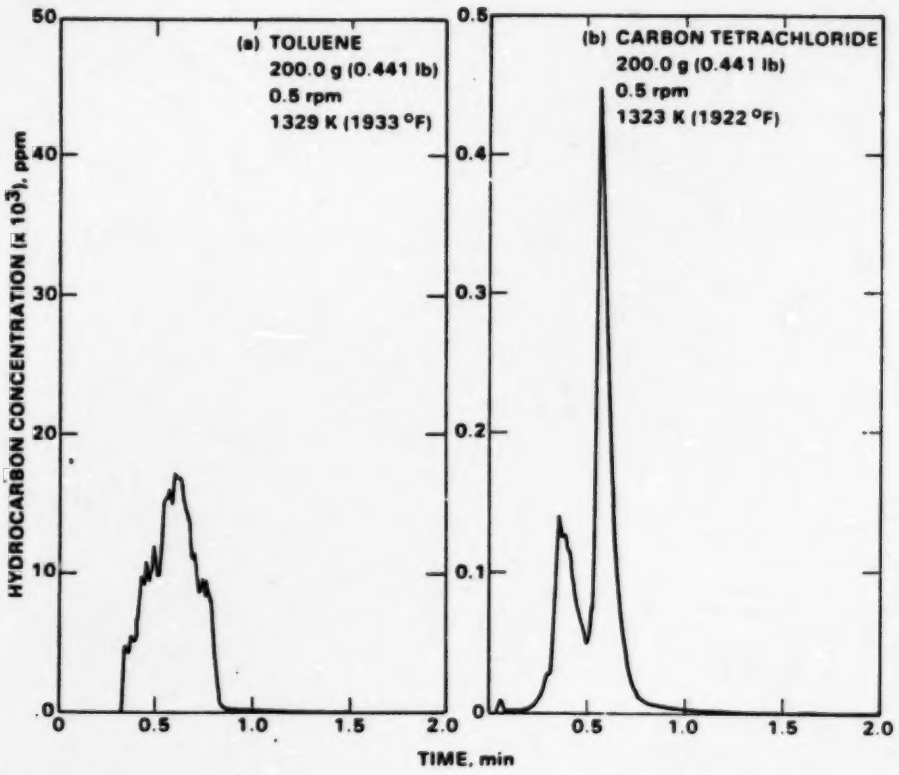

Figure 7. Comparison of toluene and carbon tetrachloride transient hydrocarbon peak shapes at similar trial conditions.

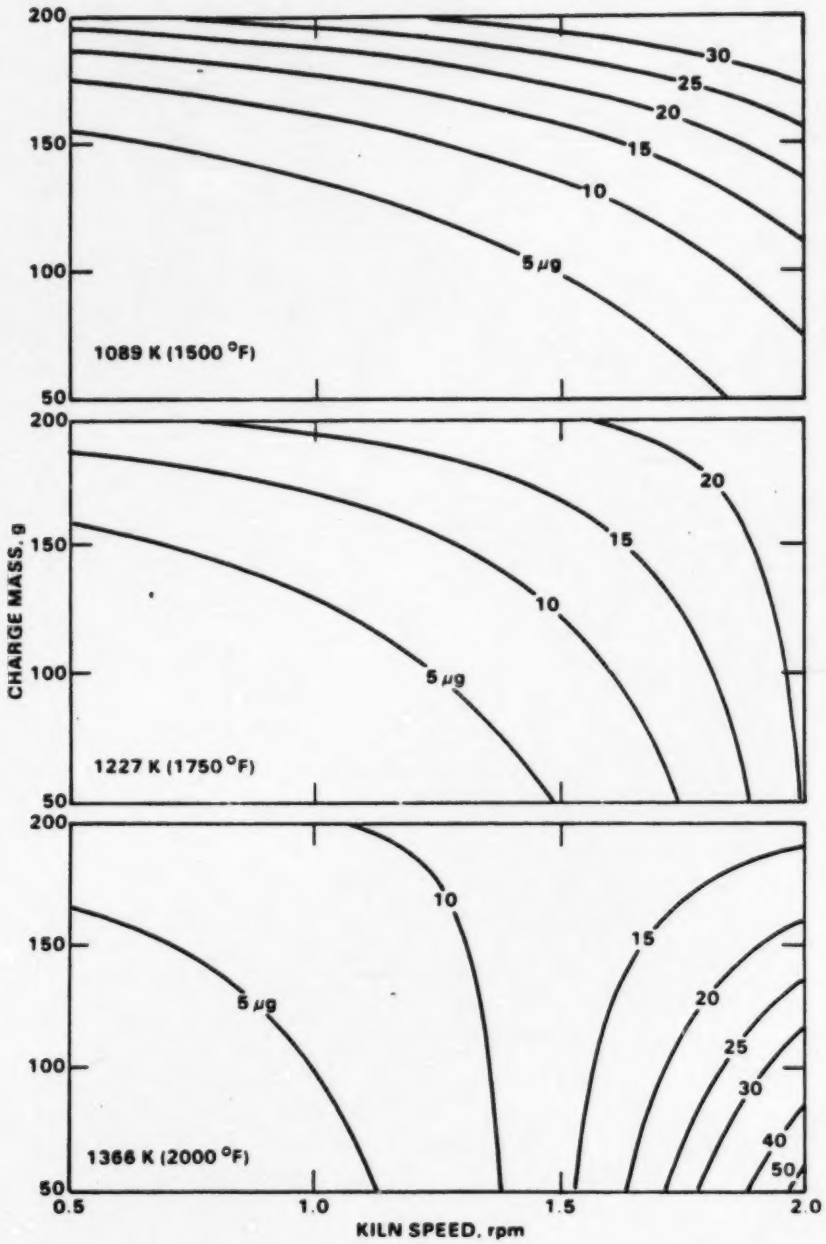

Figure 8. Effect of charge mass, kiln speed, and kiln temperature on integrated toluene peak area. (Contour values denote total volatile hydrocarbons measured as micrograms of methane.)

A non-linear model for the filter weights recorded for each test contained all the same terms as the peak area correlation except the mass-times-rotation-speed cross term. The filtered weight correlations yielded an R^2=0.9992. The resulting contour plots, shown on Figure 9, conclusively show that as kiln temperature is increased the total soot loading to the afterburner is increased; i.e., a much larger aerosol puff is formed. This result is significant and once again points to potential failure modes if the kiln is operated at too high a temperature. Contour plots for peak height of volatile (FID measurable) hydrocarbons follow the trends of those for peak area, and are not shown.

There were significant differences in the contour plots (for both peak area and filter residue mass) arising from carbon tetrachloride and those from all the other liquids. Furthermore, the CCl_4 filter residue was not black and did not resemble soot while all those of the others did. Methylene chloride filter residue masses were only slightly dependent on kiln temperature, while those for both the fuel oil and the toluene increased with kiln temperature. Peak area and peak height contours for the fuel oil do not indicate the anomalous saddle observed for the other liquids. Thus, we believe that the FID peak area and peak height contour plots of the less volatile wastes can represent the magnitude and intensity of the puff, provided these values are not too high. Toluene led to the highest peak areas, peak heights, and filter residues measured, indicating the greatest propensity to form puffs. Values for the No. 5 fuel oil were significantly lower, as were also those of the two chlorinated compounds. However, one would not expect high hydrocarbon concentrations from compounds that contain little hydrogen.

Conclusions

A laboratory rotary kiln simulator can yield useful insight into factors influencing the formation of transient puffs caused by the batch introduction of both solid and liquid wastes. The data suggest that the volatility of the waste, or rather, the rate of volatile matter release, is of paramount importance in determining the occurrence of puffs. There are therefore large differences between solid and liquid wastes and more volatile substances yield larger puffs more readily. These transients can be minimized at lower kiln temperatures, which is contrary to normal practice. Devolatilization of the waste, however, was visually

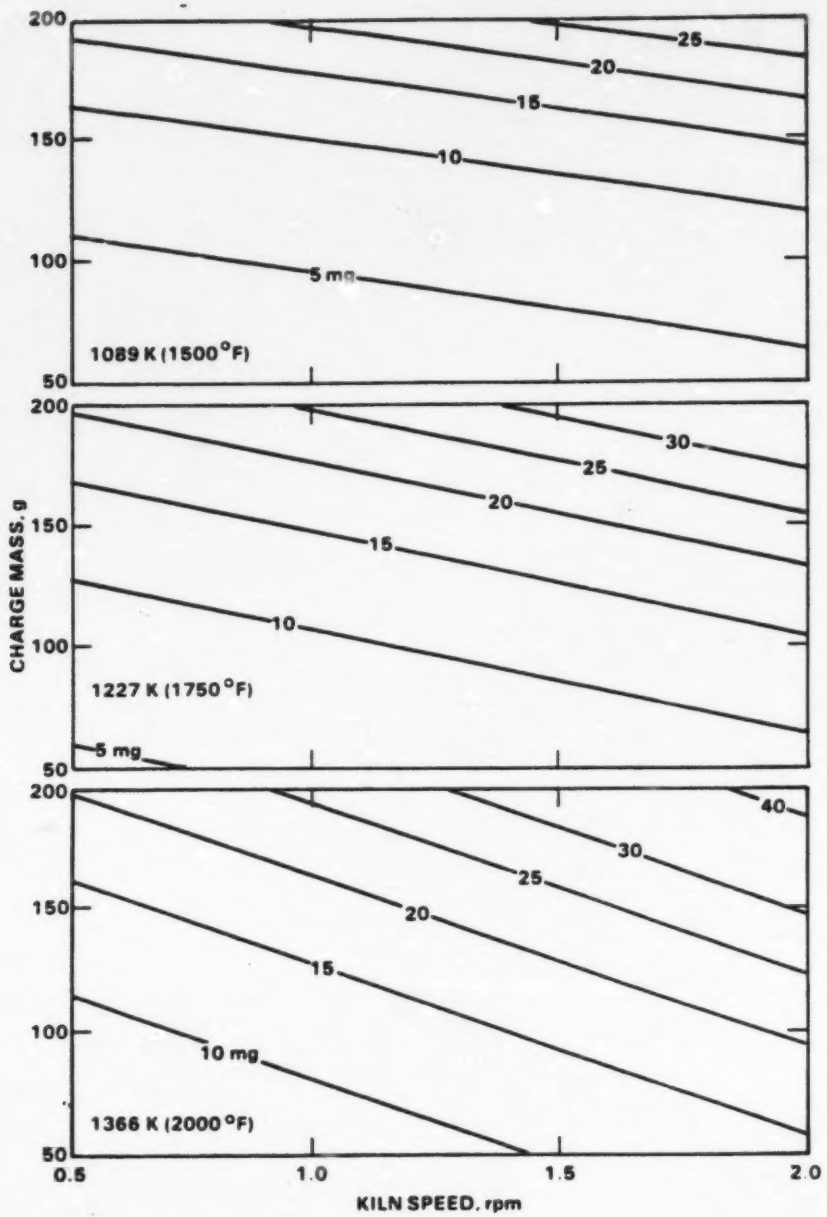

Figure 9. Effect of charge mass, kiln speed, and kiln temperature on toluene particle mass. (Contour values denote filter loadings in milligrams.)

observed to depend on many physical events occurring in the kiln, including, but not limited to, the way in which the waste contacted both the kiln walls and the flue gas from the main burner.

Transient puffs can be easily generated in the kiln and contain hazardous substances even from quite innocuous compounds such as polyethylene and polyvinylchloride. Mixtures of wastes can lead to more hazardous substances than either waste individually.

The most significant implication for practical systems is that an afterburner plays an essential role in preventing transient puffs from both solid and liquid wastes, entering the environment. Great care must be taken in the afterburner design to ensure that the puff components are then properly oxidized and destroyed. Future work could be directed at ensuring that the kiln performs more efficiently as a thermal oxidizer rather than merely as a pyrolysis furnace. This work suggests that this is not to be achieved simply by operating at high excess air, at high temperatures, and with good contacting. In fact, for the latter two variables, the converse may be true.

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References

Bonner, T.A., Cornett, C.L., Desai, B.O., Fullenkamp, J.M., Hughes, T.W., Johnson, M.L., Kennedy, E.D., McCormick, R.J., Peters, J.A., and Zanders, D.L., "Engineering Handbook for Hazardous Waste Incineration," Monsanto Research Corp., EPA-SW-889 (NTIS PB 81-248 163), U.S. EPA, Industrial Environmental Research Laboratory, Cincinnati, OH (1981).

Brunner, C., "Design of Sewage Sludge Incineration Systems," Pollution Technology Review Series No. 71, Noyes Press, Ridge Park, NJ, 239-244 (1981).

Fabian, H.W., Reher, P., and Schoen, M., "How Bayer Incinerates Waste," Hydrocarbon Processing, 4, 183-192 (1979).

Frankel, I., Sanders, N., and Vogel, G., "Survey of the Incinerator Manufacturing Industry," Chemical Engineering Progress, 3, 44-55 (1983).

Hicks, C.R., "Fundamental Concepts in the Design of Experiments," 2nd Edition, Holt, Rinehart and Winston Inc., New York, NY (1973).

James, R.H., Adams, R.E., Finkel, J.M., Miller, H.C., and Johnson, L.D., "Evaluation of Analytical Methods for the Determination of POHC in Combustion Products," Journal of the Air Pollution Control Association, 35:9, 959-969 (1985).

Johnson, L.D., and Merrill, R.G., "Stack Sampling for Organic Emissions," Toxicological and Environmental Chemistry, 6, 109-126 (1983).

Johnson, L.D., "Detecting Waste Combustion Emissions," Environmental Science and Technology, 20:3, 223-227 (1986).

Linak, W.P., Kilgroe, J.D., McSorley, J.A., Wendt, J.O.L., and Dunn, J.E., "On the Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator: I. Prototype Solid Plastic Wastes," Submitted to the Journal of the Air Pollution Control Association, June 1986.

Tanner, R.K., "Incineration of Industrial Waste," Progress in Energy and Combustion Science, 5, 245-251 (1979).